

February 1, 2008

Aging in a Structural Glass*

Walter Kob

*Institut für Physik, Johannes Gutenberg-Universität, Staudinger Weg 7, D-55099 Mainz,
Germany*

Jean-Louis Barrat

*Département de Physique des Matériaux
Université Claude Bernard and CNRS, 69622 Villeurbanne Cedex, France*

Abstract

We discuss the relaxation dynamics of a simple structural glass which has been quenched below its glass transition temperature. We demonstrate that time correlation functions show strong aging effects and investigate in what way the fluctuation dissipation theorem is violated.

PACS numbers: 61.20.Lc, 61.20.Ja, 02.70.Ns, 64.70.Pf

Typeset using REVTeX

*Talk given at STATPHYS 20, Paris, July 20-24 1998

I. INTRODUCTION

Whenever a system whose relaxation time is large is driven out of equilibrium, it can be expected that its dynamics shows aging effects. This means that observables that in equilibrium are constant become time dependent and time correlation function that in equilibrium depend only on time *differences* will now depend on *two* times. Typical examples for such situations are ferromagnetic coarsening or the relaxation dynamics of spin and structural glasses [1]. The investigation of such aging phenomena is by no means a new subject [2], but due to new theoretical approaches [1], which have led to a variety of predictions that call for being tested, this field has recently become a very active area of research.

For the case of structural glasses not much is known about the aging dynamics *on a microscopic level*, since the experiments needed to address these questions are unfortunately quite difficult. This is in contrast to computer simulations, since these easily allow to study the system on a microscopic level and thus give access to all observables of interest. The price for this advantage is that only relatively small time scales and systems can be studied, but it has turned out that these disadvantages are not too serious. In such simulations one usually mimics the experimental setup in that the system is prepared in an equilibrium state and at time zero driven out of equilibrium, e.g. by decreasing the temperature or by applying an external field. Subsequently the system is allowed to relax for a certain waiting time t_w and then one starts to measure its properties, such as the density, the magnetization or a time correlation function. This approach is also the one that we will use in the present work in an attempt of gain a better understanding of the dynamics of structural glasses at low temperatures.

II. MODEL AND DETAILS OF THE SIMULATION

For the investigation of aging effects it is useful to be able to change the waiting time over as many decades as possible and, for a given waiting time, to study the subsequent relaxation dynamics over a long time. Therefore it is advisable to study aging phenomena for models that are simple enough to be simulated over a large time window and are still reasonably realistic to catch the essential features of structural glasses. One such model is a binary Lennard-Jones mixture whose dynamical properties in its strongly supercooled state have been investigated in great detail [3]. In these studies it has been shown that the dynamics of this system can be described well by means of mode-coupling theory [4], with a critical temperature T_c around 0.435 (in reduced energy units).

The particles in this 80:20 mixture interact via a Lennard-Jones potential of the form $V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6]$ where α and β denote the type of particles (which we call “A” and “B”). In the following we will use σ_{AA} and ϵ_{AA} as the unit of length and energy, and $(m\sigma_{AA}^2/48\epsilon_{AA})^{1/2}$ as the unit of time, where m is the mass of the particles, which is independent of the species. The parameters of the potential are $\epsilon_{AA} = 1.0$, $\sigma_{AA} = 1.0$, $\epsilon_{AB} = 1.5$, $\sigma_{AB} = 0.8$, $\epsilon_{BB} = 0.5$, and $\sigma_{BB} = 0.88$. The total number of particles was 1000 and in order to minimize finite size effects we used a cubic box of size 9.4 and periodic boundary conditions. The equations of motions have been integrated with the velocity form of the Verlet algorithm with a step size of 0.02. Most of the runs were 5 million steps long.

In order to have aging phenomena a non-equilibrium situation has to be generated, which was done as follows. Starting from an equilibrium configuration at a high temperature ($T_i = 5.0$) we quenched the system at time $t = 0$ to a final temperature $T_f < T_c$. This was done by coupling the system periodically (every 50 time steps) to a heat bath. The system was allowed to evolve at the temperature T_f for the waiting time t_w and subsequently we started the measurement of the time correlation functions. In order to improve the statistics of the result this procedure was repeated 6-10 times for different initial conditions.

III. RESULTS

As shown previously in Ref. [5] quantities that, *in equilibrium*, do not depend on time, such as the total energy of the system, are not very sensitive to the aging process. Much more pronounced non-equilibrium effects are observed for time dependent quantities, such as the intermediate scattering function [5,6] or the mean squared displacement [7]. In the following we will therefore study the time and t_w dependence of $C_k(t_w + \tau, t_w)$, the generalization of the self intermediate scattering function to non-equilibrium situations. This observable is defined by

$$C_k(t_w + \tau, t_w) = \frac{1}{N} \sum_j \langle \exp[i\mathbf{k} \cdot (\mathbf{r}_j(t_w + \tau) - \mathbf{r}_j(t_w))] \rangle, \quad (1)$$

where \mathbf{k} is the wave-vector and $\mathbf{r}_j(t)$ is the position of particle j at time t . In Fig. 1 we show the time dependence of $C_k(t_w + \tau, t_w)$ for different waiting times (see figure caption). The value of $k = |\mathbf{k}|$ is 7.2, the location of the maximum in the structure factor, and $T_f = 0.4$, i.e. a temperature which is only 10% below T_c . The main figure shows C_k in a log-lin representation. We see that at short times the curves do not depend on t_w , i.e. no aging effects are observed [8]. For longer times we find, however, very pronounced aging effects in that a curve with a finite waiting time t_w starts to leave the common curve observed at short times and decays towards zero. In Ref. [5] it was shown that the time at which this peeling off from the envelope curve occurs is on the order of t_w .

In the inset we show the same data in a log-log plot. From this figure it becomes evident that at long times the relaxation of C_k is described well by a power-law with an exponent that is independent of t_w and which is around 0.4. Qualitatively similar results are found for other values of k . For short times we have found that the approach to the plateau is described well by a power-law, $C_k(t_w + \tau, t_w) \propto \tau^{-a}$, with an exponent around 0.45, a time dependence that is compatible with the prediction of mean-field theories of aging [1].

In Fig. 2 we show $C_k(t_w + \tau, t_w)$ for $t_w = 1000$ for different values of k . We see that the relaxation of the curves slows down dramatically when k is decreased. For example, the curve for $k = 3.0$ takes about 100 times longer to decay to 0.5 than the curve for $k = 6.5$. This factor has to be compared with the one expected for a diffusive process which is $(6.5/3.0)^2 \approx 4.7$, i.e. much smaller. The inset shows the same correlators in a log-log representation. From it we recognize that the time dependence of the curves is compatible with a power-law and that the exponent decreases significantly with decreasing wave-vector. (We note that for small values of k the time dependence is also compatible with a logarithmic decay, a law that is proposed from domain growth models [9].)

The results presented so far have been for the final temperature $T_f = 0.4$, i.e. a temperature that is only about 10% below the critical mode-coupling temperature of the system ($T_c = 0.435$) [3]. If the final temperature is significantly lower than T_c the relaxation behavior is qualitatively different. In Fig. 3 we show $C_k(t_w + \tau, t_w)$ for the same waiting times and the same value of k as in Fig. 1, but now for $T_f = 0.1$. A comparison of the two figures shows that the short time dynamics is qualitatively similar, except that q_{EA} , the height of the plateau at intermediate times which is called nonergodicity- or Edwards-Andersen parameter, has increased with decreasing T_f . Such a T_f dependence can easily be understood by recalling that at low temperatures this height is related to the amplitude of the vibrations of the particles in their cages and that within the harmonic approximation this amplitude is expected to be proportional to the temperature. In fact, a closer inspection of the figures shows that $1 - q_{EA}$ is indeed proportional to T_f .

The main difference between the relaxation behavior for $T_f = 0.4$ and the one for $T_f = 0.1$ occurs for long waiting times in the time regime in which the correlation functions decay below the plateau. The early stage of this decay for $T_f = 0.1$ is qualitatively similar to the one for $T_f = 0.4$. However, for very long times, $\tau > 10^4$, the correlators for $T_f = 0.1$ seem to show an additional plateau, a feature which is not present in the correlators for $T_f = 0.4$. A closer inspection of the curves for the *individual* samples (for $T_f = 0.1$ we have 9 different samples) revealed that the reason for this second plateau is given by a quite dramatic (0.1-0.2) and fast decay of the correlation function shortly before the plateau. The time at which this decay occurs depends on the sample but is usually on the order of $10^3 - 10^4$ time units. An analysis of the motion of the particles in the time range at which this sudden drop occurs shows that the decay is related to a very collective movement in which on the order of 10% of the particles move by about 0.1-0.5 units of length in one direction. This observation can be rationalized as follows. After the quench the configuration of the particles is very unfavorable and thus the system relaxes very quickly. If the system is given a bit more time, i.e. for larger waiting times, it has enough time to relax to a state which is no longer that unfavorable (for the given T_f) and hence does not relax that quickly. For intermediate and large t_w it will hence explore *for short times* τ only than part of the configuration space which corresponds to the motion of the particles within their cages. However, the system will locally still have quite large stress fields and, given enough time, will yield to these stresses and hence show a rupture like motion which is the reason for the fast drop in C_k . Since this type of motion is so abrupt it is unlikely that a mean-field like theory will be able to give a correct description of it, except perhaps in a phenomenological way. (We note that this situation is reminiscent to the one of the mode-coupling theory of supercooled liquids, since also in that case the so-called “hopping processes” strongly affect at low temperatures the very continuous, flow-like motion of the particles [4].)

A very interesting result of the theories of aging is related to the violation of the fluctuation dissipation theorem (FDT). In equilibrium the autocorrelation function $C_A(t)$ of an observable A is related to the response $R_A(t)$ of A to its conjugate field by the FDT, i.e. $R_A(t) = -(1/k_B T) \partial C(t) / \partial t$. For the non-equilibrium situation this relation is no longer valid but it can be generalized to

$$R_A(t', t) = \frac{1}{k_B T} X_A(t', t) \frac{\partial C_A(t', t)}{\partial t}, \quad (2)$$

where $t' \geq t$ and $X_A(t', t) \leq 1$ is defined by this equation. Hence $T/X_A(t', t)$ can be

considered as the temperature for which the usual connection between the time correlation function and the response holds [10]. The concept of such a temperature has been used in the glass literature for a long time, in the form of the so-called “fictive temperature”, but has remained so far a ill defined quantity. In contrast to this the definition given by Eq. (2) is from a theoretical *and practical* point of view much clearer and useful and hence more appealing. Instead of calculating the response $R_A(t', t)$ directly, where now A is the one-particle density distribution, we proceeded (basically) as follows [11]. After having quenched the system at time $t = 0$ we let it relax for a time t_w . At time t_w we applied a sinusoidal field with wave-vector k and amplitude $V_0 = 0.3$ which coupled to the density and calculated the expectation value of the density distribution [12]. Therefore we obtain the integrated response $M(t_w + \tau, t_w)$

$$V_0 M(t_w + \tau, t_w) = V_0 \int_{t_w}^{t_w + \tau} R(t_w + \tau, t) dt \quad . \quad (3)$$

It has been argued that for t_w and τ large $X_k(t_w + \tau, t_w)$ becomes a function of C_k only, i.e. $X_k(t_w + \tau, t_w) = x(C(t_w + \tau, t_w))$, where x is a function of one variable [1]. Using this and Eq. (3) we obtain

$$M(C) = \frac{1}{k_B T} \int_C^1 x(c) dc, \quad (4)$$

where we used the fact that $C_k(t_w + \tau, t_w) = 1$ for $\tau = 0$. This result suggests that a parametric plot of $k_B T M$ versus C is a useful way to look at the data and in Fig. 4 we show such a plot. For large values of C , which corresponds to short times, we see that $M(C)$ is essentially a straight line with slope close to -1.0 . This means that $x(C)$ is close to -1 , i.e. that the FDT holds. With decreasing C , corresponding to increasing time τ , the curve is compatible with a straight line with slope $-m > -1$. Therefore we find that in that region $-x(C) = m < 1$ and hence that the FDT is violated. Note that a linear dependence of M on C in the non-FDT region has also been found of “ p -spin” models [1] and thus give support to the hypotheses [13] that structural glasses are in the same universality class as such models. Finally we mention that the T_f dependence of the slope m is essentially linear. In particular we find for $T_f = 0.1$ $m = 0.1$ and for $T_f = 0.3$ and $T_f = 0.4$ $m = 0.45$ and $m = 0.62$, respectively. Assuming a linear dependence on T_f we thus expect for $T_f = T_c$ a value around 0.7, i.e. significantly smaller than 1.0, as might be expected from mean-field theory.

IV. SUMMARY

We have presented some results of a large scale computer simulation in which the non-equilibrium relaxation dynamics of a simple structural glass was investigated by quenching the system below its glass transition temperature. We find that time correlation functions, such as the generalization of the self intermediate scattering function, show a very strong dependence on the waiting time and thus are useful observables to study the aging properties of the system. We have also calculated the response function in order to investigate the violation of the FDT and have found that for short times FDT holds whereas for long

time the theorem is violated. The temperature dependence of the FDT-violation factor X is similar to the one found for certain spin glass model, thus giving evidence that at low temperatures the phase space structure of such systems is similar to the one of structural glasses. Finally we mention that many of the aging phenomena discussed here have already been observed in computer simulations and experiments on spin glasses [1] thus giving further evidence for this point of view.

Acknowledgements: We thank L. Cugliandolo, J. Kurchan, A. Latz, and G. Parisi for many useful discussions. Part of this work was supported by the Pole Scientifique de Modélisation Numérique at ENS-Lyon and the Deutsche Forschungsgemeinschaft through SFB 262.

REFERENCES

- [1] J.-P. Bouchaud, L.F. Cugliandolo, J. Kurchan, and M. Mézard, *Physica A* **226**, 243 (1996); J.-P. Bouchaud, L.F. Cugliandolo, J. Kurchan and M. Mézard in *Spin Glasses and Random Fields*, Ed.: A.P. Young (World Scientific, Singapore, 1998); H. Rieger, p. 295 in Vol. II of *Annual Reviews of Computational Physics*, Ed. D. Stauffer (World Scientific, Singapore, 1995); Th. M. Nieuwenhuizen, preprint cond-mat/9807161; A. Latz (preprint).
- [2] L. C. E. Struik, *Physical Aging in Amorphous Polymers and Other Materials* (Elsevier, Amsterdam, 1978); G. B. McKenna, p. 311 in *Comprehensive Polymer Science, Vol. 12, Polymer Properties*, Eds.: C. Booth and C. Price (Pergamon, Oxford, 1989).
- [3] W. Kob and H. C. Andersen, *Phys. Rev. E* **53**, 4134 (1995); *ibid.* **51**, 4626 (1995); *Phys. Rev. Lett.*, **73**, 1376 (1994).
- [4] W. Götze and L. Sjögren, *Rep. Prog. Phys.* **55**, 241 (1992); W. Kob, p. 28 in *Experimental and Theoretical Approaches to Supercooled Liquids: Advances and Novel Applications*, Eds.: J. Fourkas, D. Kivelson, U. Mohanty, and K. Nelson (ACS Books, Washington, 1997).
- [5] W. Kob and J.-L. Barrat, *Phys. Rev. Lett.* **78**, 4581 (1997).
- [6] J.-L. Barrat and W. Kob, preprint cond-mat/9806027.
- [7] G. Parisi, *Phys. Rev. Lett.* **79**, 3660 (1997).
- [8] Note that the small amplitude oscillations in C_k at short times stem from the periodic coupling of the system to the heat bath.
- [9] D. S. Fisher and D. Huse, *Phys. Rev. B* **38**, 373 (1988).
- [10] L. F. Cugliandolo, J. Kurchan and L. Peliti, *Phys. Rev. E* **55**, 3898 (1997).
- [11] More details on the calculation of the response can be found in Ref. [6].
- [12] We checked for the linearity of the response by varying V_0 .
- [13] T.R. Kirkpatrick and D. Thirumalai, *J. Phys. A* **22**, L149 (1989); G. Parisi, *J. Phys. A* **30**, L765 (1997).

FIGURES

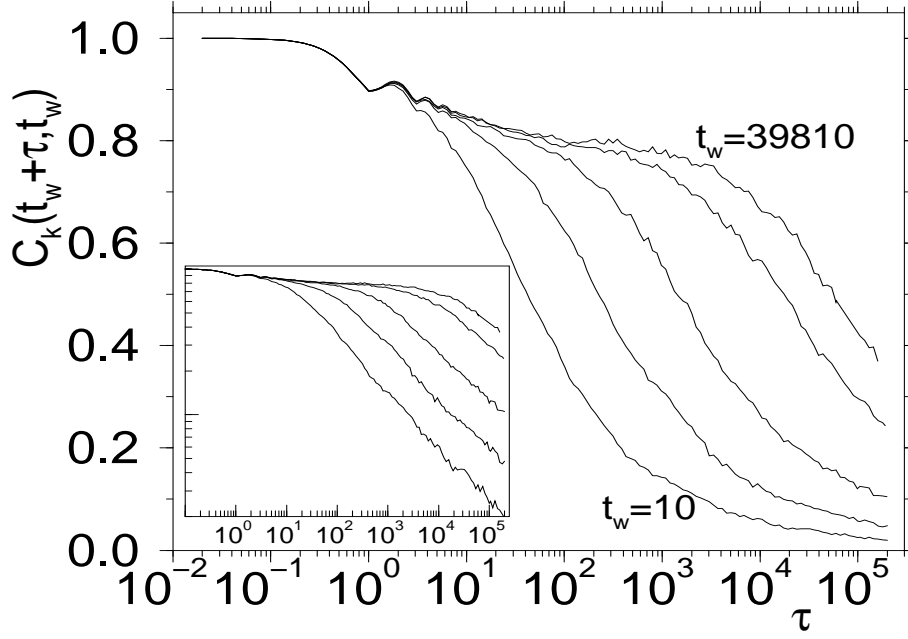


FIG. 1. Time dependence of $C_k(t_w + \tau, t_w)$ for different waiting times ($t_w = 10, 40, 1000, 10000, 39810$). $T_f = 0.4$. Inset: The same correlation functions in a double logarithmic representation.

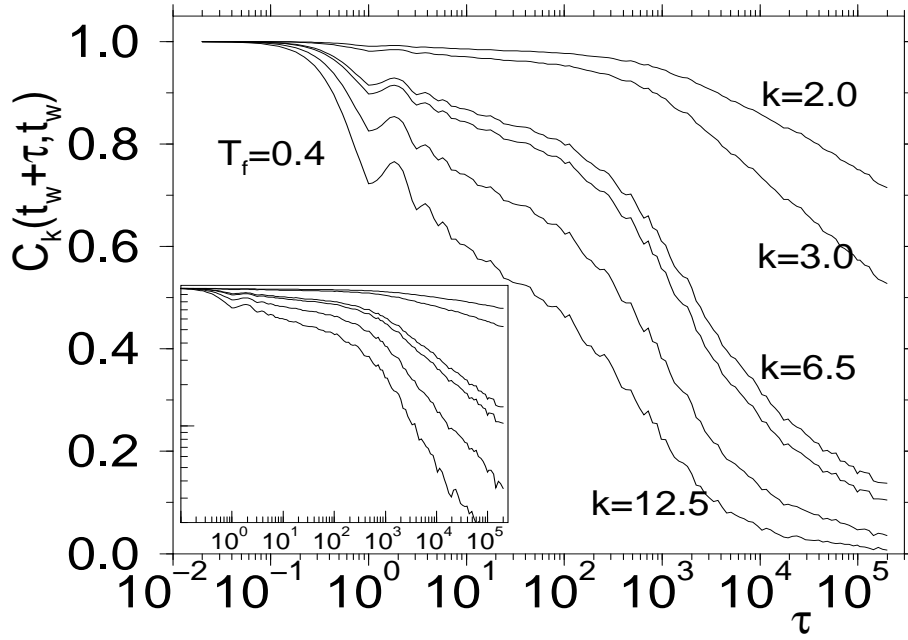


FIG. 2. Time dependence of $C_k(t_w + \tau, t_w)$ for different wave-vectors k and $t_w = 1000$. $T_f = 0.4$. From top to bottom: $k = 2.0, 3.0, 6.5, 7.2, 9.6, 12.5$. Inset: The same correlation functions in a double logarithmic representation.

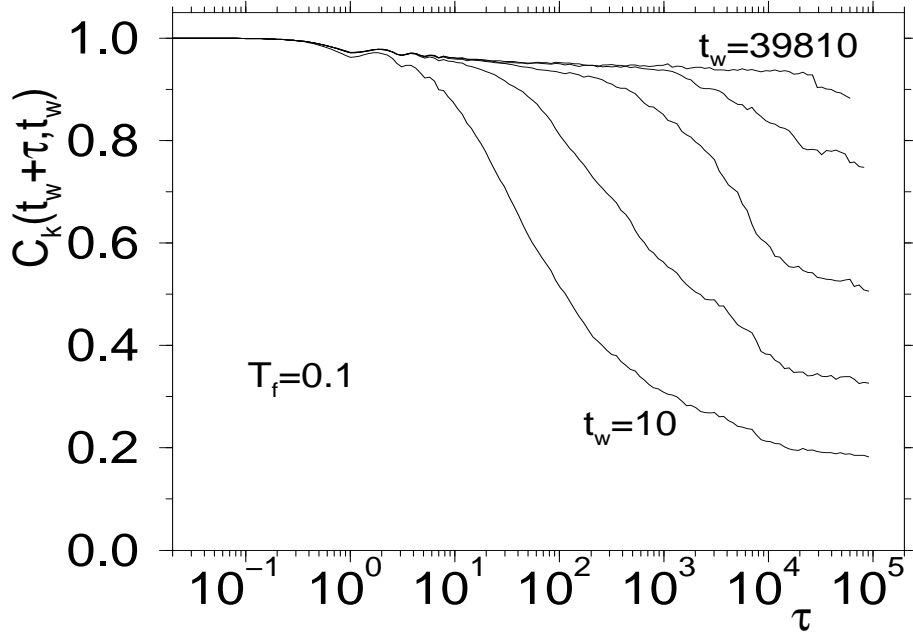


FIG. 3. Time dependence of $C_k(t_w + \tau, t_w)$ for different waiting times ($t_w = 10, 40, 1000, 10000, 39810$). $T_f = 0.1$.

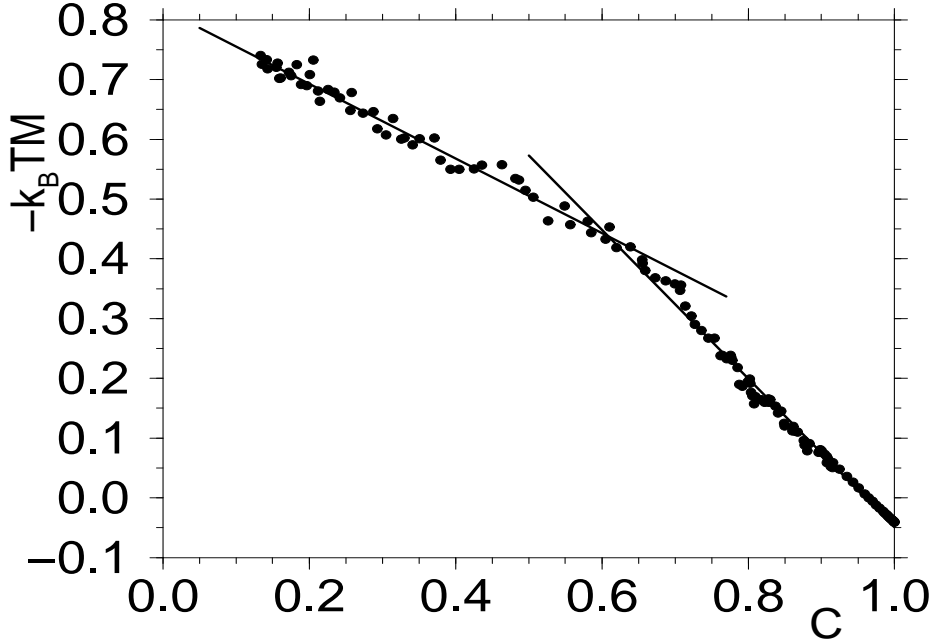


FIG. 4. Parametric plot of $-k_B T M$ versus C , where M is the integrated response. $T_f = 0.4$, $t_w = 1000$. The two straight lines have slopes around -0.62 and -1.0